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Electron-Spin-Resonance Absorption Spectrum of Platinum in Yttrium Aluminum Garnet*

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An electron-spin-resonance absorption spectrum taken at 3-cm wavelength and attributed to trivalent platinum ($5d^7$, t^6e) at octahedral sites in yttrium aluminum garnet has been observed at temperatures below 120°K. The spectrum is described by $S=\frac{1}{2}$ and $I=\frac{1}{2}$ (due to the 34% abundant ^{195}Pt). There are 24 magnetically inequivalent orientations of the platinum ion per unit cell arising from what is believed to be static Jahn-Teller distortions at each of the eight inequivalent octahedral sites. The g and A tensors are orthorhombic with principal components $g_i=1.962$, $g_j=2.361$, $g_k=2.424$ and $A_l=99$ Oe, $A_m=88$ Oe, and $A_n=30$ Oe. The two tensors are not diagonal in the same coordinate system and their orientations with respect to the garnet cubic directions is discussed.

I. INTRODUCTION

MAGNETIC resonance absorption studies have been used to examine isolated paramagnetic ions in the diamagnetic garnets both for their intrinsic interest and as a means of elucidating the properties of the ferrimagnetic garnets.[1,2] To date, such studies have been carried out on ions belonging to either the iron or rare-earth series. Results are presented here of a paramagnetic resonance investigation of isolated platinum ions, which belong to the $5d$ transition series substituted into single crystals of yttrium aluminum garnet (YAlG).

II. EXPERIMENT

Single crystals of YAlG were grown by the flux technique wherein a flux of lead salts having the YAlG ingredients is gradually cooled, causing a precipitation and growth of the crystals desired. Platinum was not intentionally introduced into the single crystals used in the present study, but most likely arose from containing the flux in platinum crucibles. Paramagnetic platinum ions were detected in some but not all of a series of crystals grown under what appeared to be similar conditions.

Paramagnetic resonance measurements were obtained using a conventional 3-cm spectrometer with superheterodyne detection.

III. RESULTS AND DISCUSSION

Platinum has a convenient identification signature in that it possesses only one isotope of nonzero nuclear spin. This is ^{195}Pt having $I=\frac{1}{2}$, which is 33.7% naturally abundant. The absorption spectrum could not be observed at temperatures above about 120°K. At 4.2°K the platinum spectrum was readily observable and found to saturate far less easily than the spectra due to trivalent iron, trivalent gadolinium, and trivalent chromium which were also present in the YAlG crystals examined. The spin-Hamiltonian parameters of the platinum spectrum, which are given in Table I, were found to be independent of temperature, as were the widths of the spectral lines which were near 7 Oe at all orientations.

With the Zeeman field applied along an arbitrary crystal direction, the fine-structure spectrum consists of 24 nearly equal intensity resonance absorption lines. When the field is confined to either the (100) or (110) planes of the crystal, these lines collapse into 12 doublets. The angular dependence of these 12 lines in the (100) and (110) planes is given in Figs. 1 and 2. In Fig. 1, the invariant line at $g_{\text{eff}}=2.36$ is found to be a superposition of four doubly degenerate lines, each of which has an angular variation of less than a linewidth. For the sake of clarity, the experimental points have been omitted from Fig. 2. Maximum degeneracy is found to occur along a crystal [100] direction where one eightfold degenerate line and one sixteen-fold de-

TABLE I. Spin-Hamiltonian g- and A-tensor principal values for platinum in YAlG.

	Principal component values	Principal component directions[a]
g_i	1.962	[0.763, 0.515, 0.391]
g_j	2.361	[0.559, 0.829, 0]
g_k	2.424	[0.324, 0.219, 0.921]
A_l	99 Oe	[0, 0.84, 0.55]
A_m	88 Oe	[1.00, 0, 0]
A_n	30 Oe	[0, 0.55, 0.84]

[a] These component directions are given with respect to the three cubic directions of the YAlG structure.

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[1] W. Low and E. L. Offenbacher, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1965), Vol. II.

[2] S. Geschwind, Phys. Rev. **121**, 363 (1961).

generate line are observed. The spectrum was fitted to a spin-Hamiltonian

$$\mathcal{H}=\beta\mathbf{H}\cdot\alpha\cdot\mathbf{S}+\mathbf{I}\cdot\mathbf{A}\cdot\mathbf{S}, \qquad (1)$$

where β is the Bohr magnetron, $\mathbf{H}$ is the Zeeman field, and $\mathbf{I}$ and $\mathbf{S}$ are the nuclear and electron spin operators, respectively.

The fine-structure data were analyzed by picking one magnetic center out of the 24 and by making measurements of its effective g value at points contained in three orthogonal planes. In the present case the $\{100\}$ planes of the cubic crystal were used. The g tensor (see Table I) was found to have orthorhombic symmetry with principal components $g_i=1.962$, $g_j=2.361$, and $g_k=2.424$ all to within an uncertainty of ± 0.001. The 24 different fine-structure components observed with the Zeeman field applied along an arbitrary direction result from one magnetic center described by this g tensor having 24 inequivalent orientations relative to the Zeeman field.

To describe these 24 orientations of the g tensor relative to the cubic axes of the crystal, it is convenient to describe first the orientation of one tensor and then to describe how the others may be obtained by systematic rotations of this tensor. Figure 3(a) shows the orientations of one g tensor relative to a set of orthogonal axes a, b, and c. These axes lie along the various $\langle 100\rangle$ axes of the crystal, that is, $\pm x$, $\pm y$, and $\pm z$; but as will be described, they are not uniquely related to specific axes of the crystal.

From Fig. 3(a) it can be seen that the directions of g_i, g_j, and g_k may be obtained from the directions of a, b, and c by making two Eulerian-angle rotations. The first of these is a rotation of 56° about the c axis, which takes the a axis into the a' axis, the latter having the direction of g_j. The second rotation of 23° about the a' axis takes the c axis into the c' axis, and defines the directions of g_k and g_i. The direction cosines of g_i, g_j, and g_k relative to the axes a, b, and c are given in Table I. These directions have uncertainties estimated at ± 1.0 degree solid angle. The 24 orientations are now obtained by associating the orthogonal axes a, b, and c used in determining the g-tensor orientation, with the different cubic axes of the garnet structure. With $[abc]$ taken in turn as $[xyz]$, $[xy\bar{z}]$, $[x\bar{y}z]$, and $[x\bar{y}\bar{z}]$, four orientations are obtained. By cyclically permuting x, y, and z the number is brought to 12. Finally, the 12 additional orientations are obtained by starting with a g-tensor orientation obtained from that shown in Fig. 3 by a reflection in the plane of a and b. Using these 24 distinct orientations and the calculated principal values of the g tensor, the angular variation of the spectrum in a crystal (100) plane was calculated and is shown as the solid lines in Fig. 1.[3]

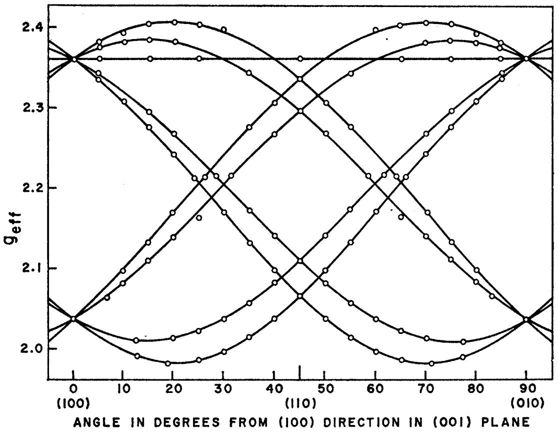

FIG. 1. Angular variation of the platinum paramagnetic resonance absorption spectrum in YAlG taken at 4.2°K with the Zeeman field confined to the (100) plane.

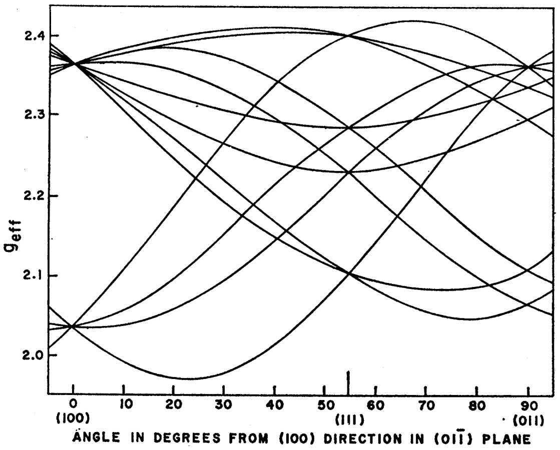

FIG. 2. Angular variation of the platinum paramagnetic resonance absorption spectrum in YAlG taken at 4.2°K with the Zeeman field confined to the (110) plane.

The 24 observed fine-structure lines can possibly be related to Pt^{1+} (d^9) ions situated at one of the 24

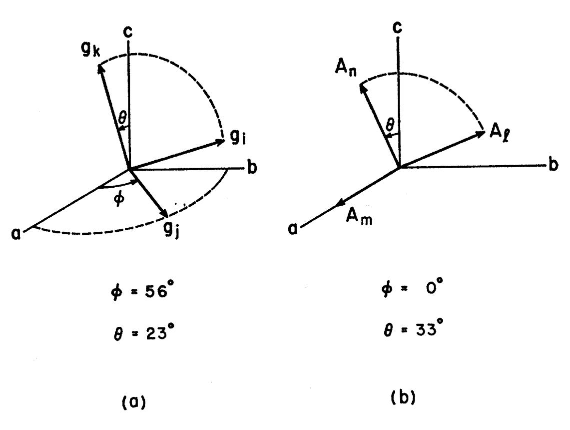

FIG. 3. Orientations of (a) the g-tensor components and (b) the A-tensor components for Pt^{3+} at one octahedral site in YAlG shown relative to a set of orthogonal axes a, b, and c.

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[3] J. E. Geusic and L. E. Brown, Phys. Rev. **112**, 64 (1958).

Table II. Comparison of the observed hyperfine splitting, in oersteds, along various crystallographic directions with those calculated from the g- and A-tensor components given in Fig. 3.

⟨100⟩ Crystal axes			⟨110⟩ Crystal axes			⟨111⟩ Crystal axes		
Direction	Obs.	Calc.	Direction	Obs.	Calc.	Direction	Obs.	Calc.
$[100]$	87	88	$[101]$	89	92	$[111]$	99	95
$[010]$	87	86	$[10\bar{1}]$	79	78	$[11\bar{1}]$	71	72
$[001]$	65	63	$[011]$	94	98	$[1\bar{1}1]$	67	63
			$[01\bar{1}]$	36	40	$[\bar{1}11]$	92	94
			$[110]$ and $[1\bar{1}0]$ were not measurable					

tetrahedral or 24 dodecahedral local sites per unit cell. The increased multiplicity of lines compared to that usually observed for ions at these sites arises from distortions of the local environment by the platinum. A more likely assignment is that the $S=\frac{1}{2}$ ground state arises from static Jahn-Teller splitting of the ^2E ground level arising from Pt^{3+} (d^7,t^6e^1) or Pt^{1+} (d^9,t^6e^3) in strong octahedral fields. The need for the strong crystalline-field approximation is consistent with that usually found to apply for ions of the 5d transition series. Because ions in garnets are usually trivalent, the assignment of Pt^{3+} is favored.

The 24 orientations of the g tensor arise from the three static Jahn-Teller distortions at each of the eight inequivalent octahedral sites per unit cell. Splitting of the ^2E level does not take place under trigonal distortion or under spin-orbit coupling but does occur under tetragonal distortion of the octahedron. However, the directions of the three orthogonal fourfold axes of the octahedron do not correspond to the observed directions of the orthorhombic g tensor.

Static Jahn-Teller distortions of Pt^{3+} in octahedral configurations have been reported previously in BaTiO$_4$ ($g_{\parallel}=1.935$, $g_{\perp}=2.51$)[4] and Al$_2$O$_3$ ($g_{\parallel}=2.011$, $g_{\perp}=2.328$).[5,6]

In the hyperfine-structure spectrum, the doublet due to ^{195}Pt is well resolved from its associated fine structure singlet at all orientations. However, because of the total number of platinum lines and their consequent overlap, it was found possible to measure the hyperfine splitting along certain directions only. Sufficient data were obtained to show that the A tensor and the g tensor are not diagonal in the same coordinate system.

Although it is not possible to associate unambiguously one specific orientation of the g tensor with a particular octahedral site in the unit cell, the association between a given orientation of the g tensor and the orientation of the A tensor corresponding to the same site in the unit cell, for example that shown in Figs. 3(a) and 3(b), is unambiguous.

Measured values of the hyperfine splitting along a number of directions in the crystal are given in Table II. This table also gives the calculated values of the hyperfine splitting obtained using the g and A tensors whose orientation and component magnitudes are given in Table I. The directions of A_l, A_m, and A_n relative to the axes a, b, and c are given in Table I. The A tensor is estimated to have an uncertainty of ±3 Oe in component magnitude with the principal axes directions uncertain to within a cone whose semi-angle is 5°. It has been considered more explicit to give the hyperfine-splitting components in this way and to use magnetic field units rather than units of energy. For example, a measurement of the hyperfine splitting along the direction of A_m will not give the magnitude value of the hyperfine splitting. It is necessary to align the magnetic moment of the ion along the direction A_m and not simply the magnetic field in this direction. The relation between the direction of the magnetic moment of an ion at a given site and the direction of the magnetic applied magnetic field is contained in a description of the g tensor for that site.

Differences in the directions of the principal axes of the g and A tensors for molecular species are not infrequent; from observed experimental data, however, such differences appear to be rare for transition metal ions.[1,7] One example that has been reported is that of tetravalent technetium (4d^3) in K$_2$PtCl$_6$.[8] In those cases where data exist for the platinum hyperfine structure, platinum in BaTiO$_3$[4] and in silicon,[9] and g and A tensors have been reported to be diagonal in the same system of coordinates.

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